

NEXAFS multiple scattering calculations of KO₂

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Since many years the oxidation of alkali metals has been attracting much interest due to the catalytic properties of metal promoters and the simple electronic structure of alkali atoms. The alkali-oxides phase diagram indicates that the interaction of oxygen with alkali metals can lead to the formation of different atomic O²⁻ ions and molecular O₂⁻ and O₂²⁻ ions. Potassium superoxide has been prepared *in situ* and high resolution O k-edge absorption NEXAFS spectra have been measured at the VUV beam-line at ELETTRA facility. The experimental data have been analyzed by multiple scattering approach deriving many geometrical and electronic details. In particular, we have found that the growth material structure is of the KO₂ type with an O-O distance of about 1.35 Å and that the transition involving single π molecular empty state of the superoxide O₂⁻ anion has a fine structure. Multiple Scattering self consistent calculation indicates that the bond between oxygen anion and K atom is totally ionic and that the fine structure is essentially due to solid state effects.

Keywords: X-ray Absorption, oxides, molecular states.

2. Introduction

The interest in the oxygen interaction with simple systems is related to the understanding of the early stages of molecular dissociation and in particular of the oxidation processes, for example of surfaces. The study of these compounds makes possible to follow the distortion of the oxygen molecule anions and the changes in molecular anion embedded in solid matrices. The amount and the nature of different ionic species is essentially controlled by the deposition procedure (Jupille et al., 1992; Asensio et al., 1987).

NEXAFS is a powerful technique to investigating the nature of the electronic empty states above the Fermi energy projected on the absorbing site. The experimental spectra contain much information both of geometrical and electronic type and their interpretation is based mainly on multiple-scattering (MS) theory in the framework of one-electron approach. On this basis many structural analysis of bulk (Benfatto et al., 1986) as well chemisorbed and gas systems (Wurth et al., 1990) have been performed in the last years.

There is no agreement in the literature on the amount of perturbation of the molecular O₂⁻ levels by the environment in alkali metal superoxides, in particular for what concerns the O-O distance. Recently NEXAFS measurements and multiple scattering calculations have been performed providing structural details on cesium-oxides compounds. The O-O distance is distorted in Cesium oxides with respect to the free ions distances (Ruckman et al., 1991). In the molecular anion CsO₂ case (Pedio et al., 1993 and 1994) the O-O distance in the results to be 1.40 ± 0.05 Å face to 1.30 Å of the

free anion case, while in the Cs₂O₂ compounds the molecular distance was found only slightly distorted.

The pure form of potassium oxides presents more difficulties to be prepared than cesium compounds. In the literature the potassium oxides has been characterized by UPS and XPS (Jupille et al., 1992) spectroscopies. Jupille and coworkers have showed that a mixture of O₂⁻ and O₂²⁻ molecular species is formed by exposure to oxygen of a K thin film.

2. Experimental

We have performed X-ray photoemission (XPS) and near-edge X-ray absorption fine structure (NEXAFS) measurements at the VUV beam line at ELETTRA (Trieste, Italy) in the Total Yield electron mode of detection, at 120 K. Figure 1 shows the O K-edge experimental NEXAFS for the co-deposited system K+O₂ compared with a CsO₂ spectrum (Pedio et al. 1993).

Potassium was evaporated from accurately out gassed SAES getter chromate sources onto a clean substrate (Si(100) or polycrystalline Cu) held at a temperature ≤ 120 K. The thickness of alkali metal films has been calibrated by the time of exposure and the K 2p core levels. In order to grow the potassium oxides two different procedures have been used (Asensio et al., 1987): in the first different exposures of O₂ (admitted through a leak valve) have been performed on a K polycrystalline film, whose thickness was above 40 Å. In the second procedure the compound has been grown *in situ*, directly on the clean substrates or on the K film by means of K deposition in oxygen atmosphere, $p_{O_2} \geq 5 \cdot 10^{-5}$ mbar. This

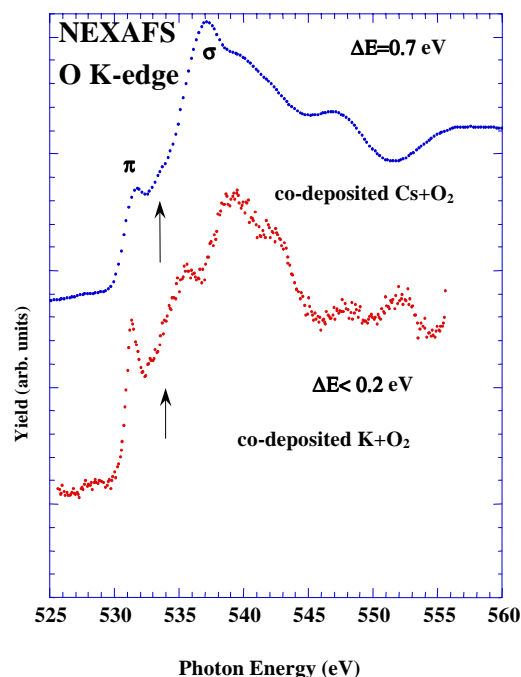


Figure 1
O K-edge of the co-deposited system K+O₂ taken at VUV Beam line and the O K-edge of CsO₂ (Pedio et al. 1993) for comparison.

procedure of growth leads to the formation of KO₂ in the first layer. A subsequent annealing at 400 K was performed in order to get a pure superoxide thin film. No differences in the experimental data have been detected using the different substrates. The experimental

spectra have been normalized to the I_0 current, simultaneously measured with the data by a copper mesh.

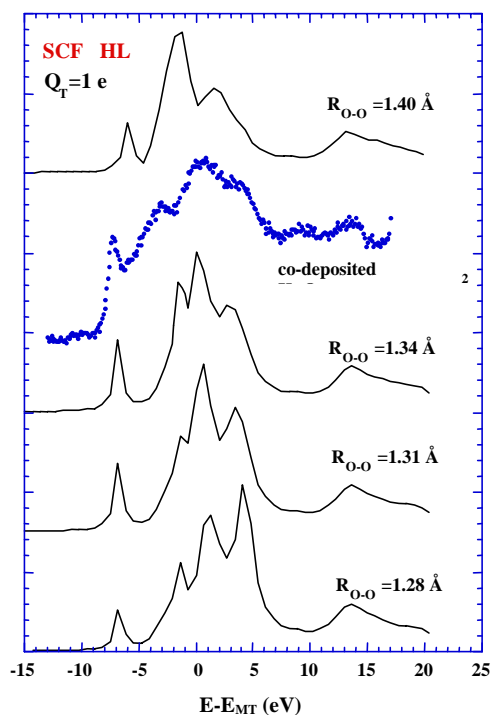


Figure 2

O K-edge of the co-deposited system K+O₂ and SCF-MS simulation performed on a cluster of KO₂ model, 83 atoms, and the O-O distance as parameter.

3. Results and discussion

Theoretical NEXAFS calculations at the O K-edge have been performed to analyze the structure of the potassium-superoxide. The cluster was built following the structure of distorted CaF₂ with the following lattice constants $a = 4.03 \text{ \AA}$ and $c = 6.69 \text{ \AA}$. The simulations were performed using the programs developed by the theory group of the Frascati laboratories using the muffin-tin approximation for the shape of the potential. Self Consistent Field (SCF) charge densities are used to describe the charge relaxation in the final state potential around the core-hole. Details on the calculation will be described in a forthcoming paper.

The comparison between experimental data and several theoretical calculations are shown in figure 2. The theoretical spectra are obtained by varying the O-O distance in the central oxygen molecule conserving the KO₂ crystal structure (our cluster is formed by 83 atoms). The different O-O distances used in the simulation are reported in the figure. Our calculations are in good agreement with the experimental data and it is also able to reproduce the transition to the π empty state of oxygen anions, the so called π resonance, which is typically located below the vacuum level, just below the rising edge. A detailed analysis of the polarization dependence of the theoretical spectra shows a xy character of this resonance confirming its assignment to a π type of resonance. Our results show that in the film grown by co-deposition, the structure of the potassium superoxide dominates. The best accordance with the experimental spectrum is achieved for an O-O distance of 1.34 \AA , particularly for what concerns the energy separation between the π and the other features. The O-O distance results slightly distorted

with respect to the distance in the free anion (1.30 \AA) but at a lower value than in CsO₂ case. These results are essentially independent from the details of the SCF procedures used in the potential generation.

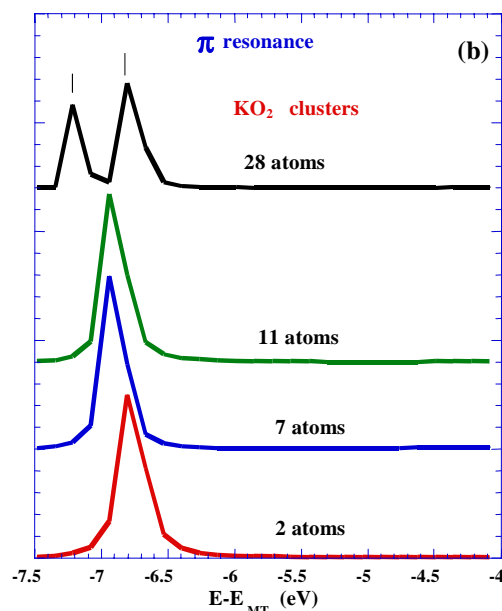
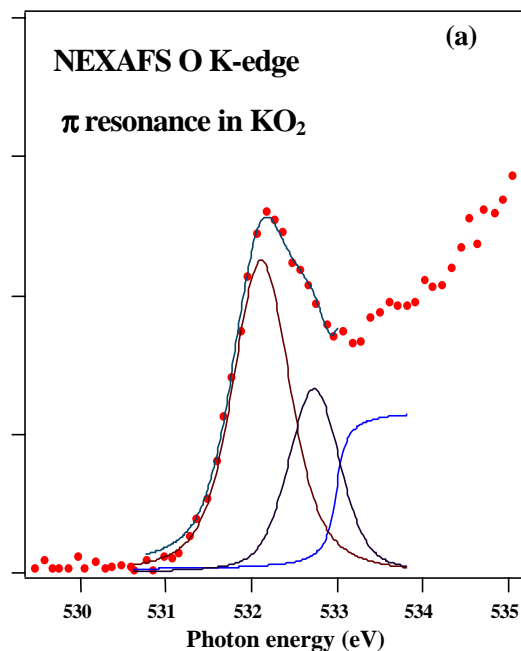


Figure 3

(a) Fit of the π resonance region in the O K-edge NEXAFS spectrum. The two Lorentzian are separated by about 0.5 eV . (b) SCF-MS calculation in the π resonance region by using different number of atoms using clusters of KO₂ geometrical type, increasing the distance from the central oxygen atom.

It is possible to conclude, as expected, that the system has a $K^+ O_2^-$ structure with a complete ionic character of the bonds between potassium and oxygen molecule. Different interpretations done on the basis of other structure models or different charge transfer from K atom to oxygen anions can be excluded.

A detailed analysis of the π resonance is reported in Fig. 3. A fine structure of the transition involving the single molecular empty state of the superoxide O_2^- anion has been found experimentally (fig 3a). A fit of the π resonance region in the O K-edge NEXAFS spectrum can be achieved by two lorentzian functions separated by about 0.5 eV. Figure 3b shows detailed SCF-MS calculations in the π resonance energy region performed by using clusters with different number of atoms around the absorber. The energy resolution is 0.12 eV. This calculation highlights the structural origin of the splitting of the π resonance essentially due to the scattering paths among other molecular anions. These results show a solid state effects never measured before on oxygen anion molecular state.

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